

MATERIAL FOR ACTIVATING POSITIVE ELECTRODE OF LITHIUM SECONDARY BATTERY AND THE LITHIUM SECONDARY BATTERY

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Inventor(s): TAKAHASHI MASAYA; TOBISHIMA SHINICHI; TAKEI KOJI; SAKURAI YOJI

Applicant(s):: NIPPON TELEGR & TELEPH CORP

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Abstract

PROBLEM TO BE SOLVED: To enhance charging and discharging capacity of a lithium secondary battery during a large-current charging and discharging, where the lithium secondary battery uses a low-price material of iron phosphate lithium as a positive electrode.

SOLUTION: A powder 2 is carried on powder 1, where a powder 1 is formed of iron phosphate lithium series material having an olivine structure, which is indicated by the general expression $LizFe_{1-y}X_yPO_4$ ($0 <= y <= 0.3$, 0). Therefore, a battery can be obtained which has larger charging and discharging capacity compared with others using an iron phosphate lithium series material that does not carry powders thereon, where charging and discharging capacity of the battery in relation to the invention is little decreased, even if charging and discharging current increases.

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(71)出願人 000004226

日本電信電話株式会社

東京都千代田区大手町二丁目3番1号

(72)発明者 高橋 雅也

東京都千代田区大手町二丁目3番1号 日

本電信電話株式会社内

(72)発明者 穂島 真一

東京都千代田区大手町二丁目3番1号 日

本電信電話株式会社内

(74)代理人 100082717

弁理士 雨宮 正季

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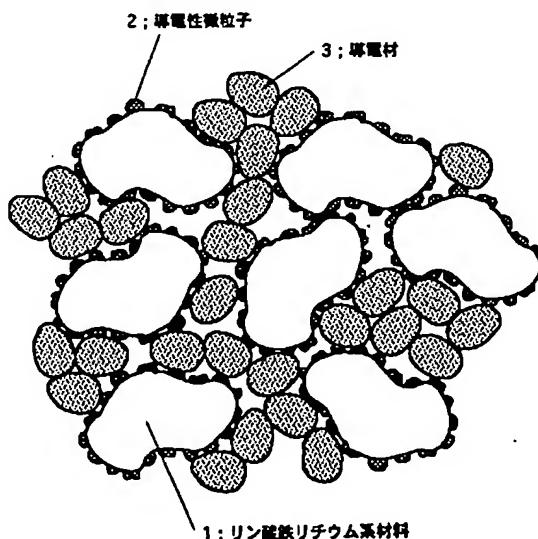
(54)【発明の名称】 リチウム二次電池正極物質およびリチウム二次電池

(57)【要約】

【課題】 安価なリン酸鉄リチウム系材料を正極に用いたリチウム二次電池の、大电流充放電時の充放電容量を高めることにある。

【解決手段】 一般式 $L i_z F e_{1-y} X_y P O_4$ ($0 \leq y \leq 0.3$, $0 < z \leq 1$ 、X:マグネシウム、コバルト、ニッケル、亜鉛の少なくとも1種類) で与えられるオリビン構造のリン酸鉄リチウム系材料粉末1上に、導電性でおかつ酸化還元電位がリン酸鉄リチウム系材料のリチウム二次電池正極物質としての酸化還元電位よりも貴な物質の粉末2を担持する。

【効果】 搅拌を行わないリン酸鉄リチウム系材料を用いた電池に比べて、充放電容量が大きくなおかつ充放電电流を増大させても充放電容量の減少が少ない電池が得られる。



【特許請求の範囲】

【請求項1】 一般式 $Li_xFe_{1-y}X_yPO_4$ ($0 \leq y \leq 0.3$, $0 < z \leq 1$, X: マグネシウム、コバルト、ニッケル、亜鉛の少なくとも1種類) で与えられるオリビン構造のリン酸鉄リチウム系材料粉末上に、導電性でおかつ酸化還元電位が、リン酸鉄リチウム系材料のリチウム二次電池正極活物質としての酸化還元電位よりも貴な導電性微粒子を担持したことを特徴とするリチウム二次電池正極活物質。

【請求項2】 前記導電性微粒子が、銀、炭素、白金、パラジウム、金、イリジウム、アルミニウム、チタン、タンタルの少なくとも1種類であることを特徴とする請求項1記載のリチウム二次電池正極活物質。

【請求項3】 請求項1あるいは2記載のリチウム二次電池正極活物質を正極活物質とし、さらにリチウム金属、リチウム合金またはリチウムイオンを吸蔵、放出可能な物質を負極活物質とし、またリチウムイオンが前記リチウム二次電池正極活物質や前記負極活物質と電気化学反応をするための移動を行いうる物質を電解質として含むことを特徴とするリチウム二次電池。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明はリチウム二次電池正極活物質およびリチウム二次電池に関し、特に正極活物質の導電性向上に関わり、電池の大電流での放電特性あるいは充電特性の改善を目指すものである。

【0002】

【従来の技術】 リチウム金属、リチウム合金あるいはリチウムイオンを吸蔵、放出可能な物質を負極活物質とするリチウム二次電池は高い電圧と優れた可逆性を特徴としている。

【0003】 特に正極活物質としてリチウムと遷移金属との複合酸化物を用い、負極活物質として炭素系材料を用いたリチウムイオン二次電池は、従来の鉛二次電池やニッケルーカドミウム二次電池などに比べ軽量で放電容量も大きいことから、携帯電話やノート型パソコンなどの電子機器に広く使用されている。

【0004】 現在一般に用いられているリチウムイオン二次電池の正極活物質としては、主に $LiCoO_2$ が用いられているが、 $LiCoO_2$ の原料であるコバルトは埋蔵量が少なく、しかも限られた地域でしか産出しないため、今後、より一層の需要増加が見込まれるリチウムイオン二次電池の正極活物質としては、価格の面からも原料の安定供給の面からも好ましくない。

【0005】 これに対して、産出量が多く安価な鉄を原料に用いた $LiFePO_4$ あるいは $LiFePO_4$ の鉄の一部を他元素で置換した材料がリチウム二次電池の正極活物質として動作することが特開平9-134724号、特開平9-134725号、特願平11-261394号などにより明らかにされている。

【0006】

【発明が解決しようとする課題】 しかし、これらのリン酸鉄リチウム系材料は電池充放電時のリチウムの挿入脱離反応が遅く、しかも従来用いられてきた $LiCoO_2$ などのリチウム金属酸化物に比べて電気抵抗が大きいため、大きな電流で充放電を行った場合に抵抗過電圧や活性化過電圧が増大し、電池の電圧が低下してしまうため、十分な充放電容量が得られないという問題がある。

【0007】 この様な問題を解決する方法として、リン酸鉄リチウム系材料の粒子を微細化し、反応が進行する面積を増やすと共に、電流がリン酸鉄リチウム系材料粒子内部を流れる距離を短くすることが考えられる。

【0008】 しかし、リン酸鉄リチウム系材料の微細な粒子は電極作製時に導電材と混合する際に二次凝集を起こしやすい。凝集粒内部ではリン酸鉄リチウム系材料粒子同士が小さな点で接触しているために電気抵抗が非常に大きくなることから、凝集粒中央部の活物質では電池の充放電を行っても反応が起こらず、充放電容量が低下してしまう。

【0009】 従って、本発明は前述した従来の課題を解決するためになされたものであり、その目的は、安価なリン酸鉄リチウム系材料を正極に用いたリチウム二次電池の、大電流充放電時の充放電容量を高めることにある。

【0010】

【課題を解決するための手段】 この様な目的を達成するために、本発明によるリチウム二次電池正極活物質は、一般式 $Li_xFe_{1-y}X_yPO_4$ ($0 \leq y \leq 0.3$, $0 < z \leq 1$, X: マグネシウム、コバルト、ニッケル、亜鉛の少なくとも1種類) で与えられるオリビン構造のリン酸鉄リチウム系材料粉末上に、導電性でおかつ酸化還元電位がリン酸鉄リチウム系材料のリチウム二次電池正極活物質としての酸化還元電位よりも貴な物質の粉末を担持することを特徴とするものである。

【0011】 また、本発明によるリチウム二次電池正極活物質は、前記の導電性でおかつ酸化還元電位がリン酸鉄リチウム系材料のリチウム二次電池正極活物質としての酸化還元電位よりも貴な物質が、銀、炭素、白金、パラジウム、金、イリジウム、アルミニウム、チタン、タンタルの少なくとも1種類であることを特徴とするものである。

【0012】 さらに、本発明によるリチウム二次電池は、上述したリチウム二次電池正極活物質を含み、さらにリチウム金属、リチウム合金またはリチウムイオンを吸蔵、放出可能な物質を負極活物質として、またリチウムイオンが前記正極活物質や前記負極活物質と電気化学反応をするための移動を行いうる物質を電解質として含むことを特徴とするものである。

【0013】 図1は、本発明によるリチウム二次電池に用いられる正極活物質と導電材を混合して作製した正極

の一部を拡大した断面の模式図である。この図より明らかなように、リン酸鉄リチウム系材料粉末1の表面に導電性微粒子2を担持することにより、リン酸鉄リチウム系材料粉末同士が直接接触する部分がほとんど無くなり、リン酸鉄リチウム系材料粉末1の粒径を小さくしても電極作製時に導電材3と混合した際の凝集が起こりにくくなる。

【0014】さらにリン酸鉄リチウム系材料粉末1が凝集した場合にも凝集粒内部に導電性微粒子2による電流の経路が形成されるため、凝集粒内部の電気抵抗が大幅に低減され、電池を大電流で充放電した際にも凝集粒内部の活物質が十分に利用されるようになることから、リン酸鉄リチウム系材料粉末1の凝集による充放電容量の低下が抑止される。

【0015】また、従来のリチウム二次電池正極においては、電気抵抗の大きな活物質粒子同士あるいは活物質粒子と導電材粒子が直接接触していたため、接触面積の小さな部分では大きな抵抗が生じてしまっていたが、本発明の正極活物質では導電性微粒子2同士あるいは導電性微粒子2と導電材3が接触しているため、活物質と導電材3の接触面における抵抗が小さくなるとともに、電池の充放電を繰り返した際の活物質の膨張収縮により、接触面積が変化した場合の抵抗の変化も小さくなり、大電流で充放電を行った場合のエネルギー損失が小さくなるとともに充放電に伴う容量劣化も少なくなる。これらの効果が複合することにより、本発明の正極活物質を用いることによりリン酸鉄リチウム系材料を正極活物質に用いたリチウム二次電池の大電流での充放電時の充放電容量が増加すると考えられる。

【0016】本発明によるリチウム二次電池正極活物質のリン酸鉄リチウム系材料は、一般式 $\text{Li}_z\text{Fe}_{1-y}\text{X}_y\text{PO}_4$ ($0 < z \leq 1$, $0 < y \leq 0.3$) で与えられるオリビン構造のリン酸化合物で、元素Xは該リン酸化合物を構成している状態では、リチウム金属の標準電位に対して3Vから4Vの電位領域で電気化学的に安定な物質である。すなわち、Xはマグネシウム、コバルト、ニッケル、亜鉛の少なくとも1種類である。図2に LiFePO_4 のオリビン構造を示す。黒丸がリチウム原子を、八面体は6個の酸素で囲まれた鉄を、四面体は4個の酸素で囲まれたリンをそれぞれ示している。

【0017】上述の様な一般的にリン酸鉄リチウムと呼ばれている物質は LiFePO_4 ($z=1$, $y=0$) で表され、構造を保ったままでリチウムをこれ以上挿入することはできない。このリン酸鉄リチウム系材料を電池の正極として用いた場合、充電を行うとリチウムが正極から抜けて行き、組成は FePO_4 に近づき (z が小さくなる)、充電した電池を放電すると、電解液中のリチウムが正極中に挿入され、組成が LiFePO_4 ($z=1$) に戻っていく。電池の放電容量や作製を考えると $z=1$ の材料が最も好ましいが、この様に z の値は連続的

に変化するため、不定比な組成である $z=0.9$ などの組成の物質でも、一般的な定比の組成である $z=1$ のリン酸鉄リチウムと同等の機構で動作する電池が作成可能である。このため、上記式中、 z は $0 < z \leq 1$ で示される。

【0018】 LiFePO_4 は、その充電の際にリチウムが脱離するとともに鉄イオンが2価から3価に変化する。リチウムが脱離した結果、その部分の結晶構造(オリビン構造)が不安定になり部分的にリチウムの移動経路が塞がれてしまい、更に内部にあるリチウムが脱離しにくくなる。リン酸化合物を構成している状態でリチウム金属の標準電位に対して3Vから4Vの電位領域で電気化学的に安定な亜鉛等の元素で一部の鉄を置き換えると、充電を行っても亜鉛等の置換した元素は2価のままで酸化されず、置換した元素に隣接するリチウムも脱離せずに結晶内に残る。このため、充電を行っても置換を行った部分は結晶構造が変化しにくく、リチウムの移動経路が確保されたために容量が増大すると共にサイクル安定性を向上させるものと考えられる。しかし、脱離しないリチウムは充放電に関与しないため、この様な置換をあまり多く行うと電池の容量が減少してしまう。このため、鉄元素を置換する場合には、容量増加の効果が見られる鉄元素の置換量は30% ($0 \leq y \leq 0.3$) 以下、好ましくは10%~30% ($0.1 \leq y \leq 0.3$)、さらに好ましくは10~20% ($0.1 \leq y \leq 0.2$) であるのがよい。

【0019】本発明においては、リン酸鉄リチウム系材料の表面に前記の導電性でなおかつ酸化還元電位がリン酸鉄リチウム系材料のリチウム二次電池正極活物質としての酸化還元電位よりも貴な(高い)導電性微粒子を付着せしめるものである。これはリチウム二次電子内において導電性微粒子の電気化学反応が起こる電位がリン酸鉄リチウム系材料の酸化還元電位(約3.4V)より低いと、前記導電性微粒子が先に電気化学反応を生じてしまい、酸化による溶解か導電性の低下が起こり、導電性微粒子担持の効果が失われてしまうからである。

【0020】この様な導電性微粒子としては、たとえば銀、炭素、白金、パラジウム、金、イリジウム、アルミニウム、チタン、タンタルの少なくとも1種類であるのが好ましい。後述の実施例においては前記導電性微粒子として、金属材料としては銀、パラジウム、白金を、また炭素材料としてはアセチレンブラックを用いたが、この他に金属材料としては金、イリジウム、アルミニウム、チタン、タンタルなどでもよい。また、炭素材料としてはグラファイトやケッテンブラックでも構わない。

【0021】さらに導電性微粒子の添加量としては、この物質自体が充放電反応に関与しないことから、添加量を増やしすぎるとリン酸鉄リチウム系材料と導電性微粒子を併せた正極活物質全体としての単位重量あるいは単

位体積当りの放電容量が減少するため、10%以下が好ましく、特に2%~6%が好ましい。

【0022】また導電性微粒子の粒径としては、リン酸鉄リチウム系材料粉末の粒径の1/10以下が好ましく、特に1/100以上1/10以下が好ましい。導電性微粒子は電池反応に関与しないため、リン酸鉄リチウム系材料粉末表面に、なるべく少ない重量で、まんべんなく付着せしめるのが好ましい。このため導電性粒子の粒径が大きくなると、前記リン酸鉄リチウム系材料粉末表面に、まんべんなく付着させると、導電性粒子の量が多くなりすぎて、エネルギー密度の低下を招く恐れがあるからである。

【0023】さらに後述の実施例において、正極としてはペレット状に成型したものを用いたが、N-メチル-2-ピロリドンの様な溶媒に正極活物質とポリフッ化ビニリデンの様なバインダを加えてスラリーを作製し、それを金属箔上に薄く塗布乾燥した塗布電極の様な形状でも構わない。

【0024】また、負極材料としてはリチウム金属を用いたが、他にリチウム合金、黒鉛やコークスなどの炭素系材料、タングステン酸化物、ニオブ酸化物、バナジウム酸化物、スズ酸化物などの金属酸化物、リチウムマンガン窒化物やリチウムコバルト窒化物、リチウム鉄窒化物などのリチウム遷移金属複合窒化物、硫化鉄や硫化モリブデン等の金属カルコゲナイトなどでも構わない。

【0025】さらに電解液としてはエチレンカーボネートとジメチルカーボネートの等積混合溶媒にLiPF₆を1mol/dm³濃度に溶解した電解液を用いたが、従来の非水系リチウム二次電池と同様なものも使用可能である。

【0026】例えば溶媒としてはジメトキシエタン、2-メチルテトラヒドロフラン、エチレンカーボネート、メチルホルムエート、ジメチルスルホキシド、プロピレンカーボネート、アセトニトリル、ジメチルカーボネート、ジエチルカーボネート、メチルエチルカーボネートなどを単独で、あるいは2種類以上を混合して使用することが可能である。

【0027】また、溶質としては実施例において用いたLiPF₆以外にも、例えば、LiClO₄、LiBP₄、LiAsF₆、LiCF₃SO₃等でも構わない。更に、ポリマー電解質、固体電解質、常温溶融塩等も使用可能である。

【0028】また、セパレータや電池ケース等の構造材料等の他の要素についても従来公知の各種材料が使用可能である。さらに電池形状についても実施例においてはコイン型としたが、特に制限されるものではなく、円筒型、角型等の形状でもかまわない。

【0029】

【実施例】以下に、図面を参照して本発明の実施例をより詳細に説明する。なお、本発明は以下の実施例のみに

限定されるものではない。

【0030】

【実施例1】図3は本発明によるリチウム二次電池の一実施例による構成を示した電池断面図である。図3において、4は正極ペレット、5は金属リチウム負極、6はセパレータ、7は正極ケース、8は封口板、9はガスケットである。正極ペレット4に含まれる正極活物質は下記の方法で作製した。

【0031】まずLiFePO₄を原料である炭酸リチウム(Li₂CO₃)と、シュウ酸鉄2水和物(FeC₂O₄·2H₂O)と、リン酸水素二アンモニウム((NH₄)₂HPO₄)をモル比で0.5:1:1となるように混合して坩堝に入れ、アルゴン雰囲気下で800°Cで24時間焼成することにより合成した。

【0032】次いで、水とエタノールを体積比で1:1に混合した溶液中に合成したLiFePO₄粉末を入れ十分に攪拌し、攪拌を続けながら硝酸銀(AgNO₃)を、含まれる銀イオンの重量がLiFePO₄の重量の5%となるよう秤量して加えた。

【0033】更に攪拌を続けながらアセトアルデヒドを、AgNO₃ 1g当たり20ml加えてLiFePO₄粉末上に銀を析出させた。これをろ過、乾燥することにより正極活物質を作製した。

【0034】得られた正極活物質のX線回折チャートを図4に示す。LiFePO₄のピークに加え、図4中に*で示した金属状態の銀のピークが観察された。また電子顕微鏡観察とEPMA測定により、LiFePO₄粉末上にLiFePO₄粉末の粒径の約1/20の粒径の銀の微粒子が分散担持していることを確認した。

【0035】この正極活物質70重量%と導電材であるアセチレンブラック25重量%及び結着剤であるポリテトラフルオロエチレン5重量%を混練し、粘土状の塊としたものを2軸ローラーで厚さ0.6mm程度に圧延してからポンチで直径15mmの円板状に打ち抜いて正極ペレット4を作製した。

【0036】次にステンレス製の封口板8上に金属リチウム負極5を加圧配置したものをポリプロピレン製ガスケット9の凹部に挿入し、負極の上にポリプロピレン製で微孔性のセパレータ図6、正極ペレット4をこの順序に配置し、電解液として、エチレンカーボネートとジメチルカーボネートの等積混合溶媒にLiPF₆を1mol/dm³の濃度に溶解した電解液を適量注入して含浸させた後に、ステンレス製の正極ケース7を被せてかしめることにより、厚さ2mm、直径23mmのコイン型リチウム二次電池を作製した。

【0037】作製した電池の充放電特性を充電終止電圧4.0V、放電終止電圧3.0V、1mA及び電流の大きさ5mAの定電流という条件で充放電を行うことにより評価した。

【0038】5mAの電流で放電した際の電圧曲線を図

5に示す。電圧曲線は、既に知られている導電性の微粒子を担持していないリン酸鉄リチウムを正極に、リチウム金属を負極に用いた電池を小さな電流で充放電した際の電圧とほぼ同一であり、鉄イオンの酸化還元により充放電が行われ、担持した導電性材料の酸化還元は起こっていないことが確認された。

【0039】放電容量は、電流1mAの場合が5.6mA·h、電流5mAの場合が4.3mA·hであった。それぞれの電流値で充放電試験を行った際の放電容量を表1に示す。

【0040】

【表1】

実施例及び比較例に示した電池の放電電圧と放電容量

実施例及び比較例	1mA放電時の放電容量(mA·h)	5mA放電時の放電容量(mA·h)
実施例1	5.6	4.3
比較例1	5.2	3.6
実施例2	5.7	4.4
実施例3	5.4	4.0
実施例4	5.5	4.1

【0041】

【比較例1】導電性物質の担持処理を行わない正極活物質であるLiFePO₄を下記の方法で作製した。

【0042】まず原料である炭酸リチウム(Li₂CO₃)と、シュウ酸鉄2水和物(FeC₂O₄·2H₂O)と、リン酸水素二アンモニウム((NH₄)₂HPO₄)をモル比で0.5:1:1となるように混合して坩堝に入れ、アルゴン雰囲気下で800°Cで24時間焼成することにより作製した。

【0043】得られた正極活物質を用いて実施例1と同一の方法により正極ペレット及びコイン型電池を作製した。

【0044】実施例1と同一の条件で充放電特性を評価したところ、放電容量は、電流1mAの場合が5.2mA·h、電流5mAの場合が3.6mA·hであり、いずれの場合も実施例1より小さな放電容量しか得られず、特に5mAの定電流で試験した場合の容量の低下が大きかった。

【0045】5mAの電流で放電した際の電圧曲線を実施例1の曲線と併せて図4に示す。また、それぞれの電流値で充放電試験を行った際の放電容量を実施例1の値と併せて表1に示す。

【0046】

【実施例2】正極ペレットに含まれる正極活物質を下記の方法で作製した。

【0047】まず原料である炭酸リチウム(Li₂CO₃)と、シュウ酸鉄2水和物(FeC₂O₄·2H₂O)と、リン酸水素二アンモニウム((NH₄)₂HPO₄)をモル比で0.5:1:1となるように混合して坩堝に入れ、アルゴン雰囲気下で350°Cで5時間焼成した。

【0048】次いで、アセチレンブラック(電気化学工業製)を原料1kg当たり10g加え、十分に混合した後、アルゴン雰囲気下で800°Cで24時間焼成するこ

とにより作製した。

【0049】得られた正極活物質を用いて実施例1と同一の方法により正極ペレット及びコイン型電池を作製した。

【0050】実施例1と同一の条件で充放電特性を評価したところ、放電容量は、電流1mAの場合が5.7mA·h、電流5mAの場合が4.4mA·hであり、いずれの場合も比較例1より大きな放電容量が得られた。

【0051】それぞれの電流値で充放電試験を行った際の放電容量を実施例1及び比較例1の値と併せて表1に示す。

【0052】

【実施例3】正極ペレットに含まれる正極活物質を下記の方法で作製した。

【0053】まずLiFePO₄を原料である炭酸リチウム(Li₂CO₃)と、シュウ酸鉄2水和物(FeC₂O₄·2H₂O)とリン酸水素二アンモニウム((NH₄)₂HPO₄)をモル比で0.5:1:1となるよう混合して坩堝に入れ、アルゴン雰囲気下で800°Cで24時間焼成することにより合成した。

【0054】次いで、酢酸パラジウム(Pd(OCOCH₃)₂)のアセトニトリル溶液中に合成したLiFePO₄を粉碎した後に加えて十分に攪拌した後、ろ過、乾燥し、LiFePO₄粉末上にPd(OCOCH₃)₂を付着させた。

【0055】これをアルゴン雰囲気下で250°Cで5時間焼成し、Pd(OCOCH₃)₂を熱分解することでLiFePO₄粉末上にパラジウムを担持することにより正極活物質を作製した。

【0056】得られた正極活物質を用いて実施例1と同一の方法によりコイン型電池を作製した。

【0057】実施例1と同一の条件で充放電特性を評価したところ、放電容量は、電流1mAの場合が5.4mA·h

A h、電流5 mAの場合が4.0 mA hであり、いずれの場合も比較例1より大きな放電容量が得られた。

【0058】それぞれの電流値で充放電試験を行った際の放電容量を実施例1、2及び比較例1の値と併せて表1に示す。

【0059】

【実施例4】正極ペレットに含まれる正極活物質を下記の方法で作製した。

【0060】まず原料である水酸化リチウム1水和物($\text{LiOH} \cdot \text{H}_2\text{O}$)と、ショウ酸鉄2水和物($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$)と、リン酸水素二アンモニウム($(\text{NH}_4)_2\text{HPO}_4$)をモル比で1:1:1となるように混合して坩堝に入れ、アルゴン雰囲気下で800°Cで24時間焼成し LiFePO_4 を合成した。

【0061】次いで、得られた LiFePO_4 粉末に LiFePO_4 100 g当たり6 gの白金粉末(300メッシュ)を加え、乳鉢で混合した後に瑪瑙製遊星ボルミルに入れ、20分間粉碎混合して LiFePO_4 粉末上に白金の微粒子を分散担持した。

【0062】得られた正極活物質を用いて実施例1と同一の方法によりコイン型電池を作製した。

【0063】実施例1と同一の条件で充放電特性を評価したところ、放電容量は、電流1 mAの場合が5.5 mA h、電流5 mAの場合が4.1 mA hであった。それぞれの電流値で充放電試験を行った際の放電容量を実施例1から3及び比較例1の値と併せて表1に示す。

【0064】

【発明の効果】以上説明したように、本発明によるリチウム二次電池によれば、正極活物質として、リン酸鉄リチウム系材料粉末上に導電性を有する微粒子を担持した物質を用いることにより、担持を行わないリン酸鉄リチウム系材料を用いた電池に比べて、充放電容量が大きくなおかつ充放電電流を増大させても充放電容量の減少が少ない電池が得られることを見いたした。

チウム系材料粉末上に導電性を有する微粒子を担持した物質を用いることにより、担持を行わないリン酸鉄リチウム系材料を用いた電池に比べて、充放電容量が大きくなおかつ充放電電流を増大させても充放電容量の減少が少ない電池が得られることを見いたした。

【0065】従って経済的に優れて、なおかつ電池特性の良好なりチウム二次電池の実現が可能となった。

【図面の簡単な説明】

【図1】本発明によるリチウム二次電池正極活物質と導電材を混合して作製した正極の一部を拡大した断面模式図。

【図2】オリビン構造を示す模式図。

【図3】本発明によるリチウム二次電池の一実施例による構成を示した断面図。

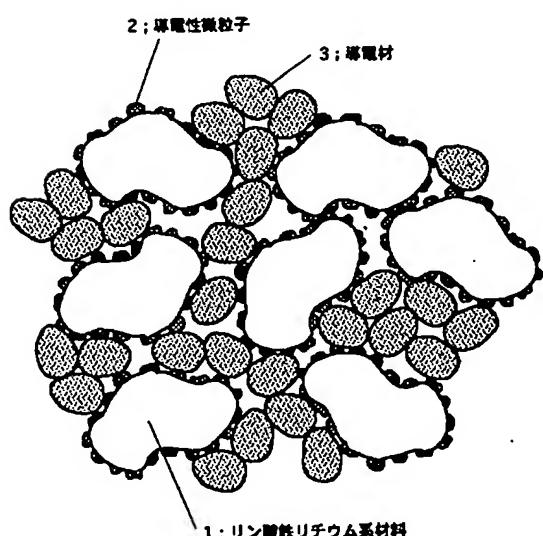
【図4】本発明のリチウム二次電池の実施例1において正極活物質として用いた、銀微粒子を表面に担持した LiFePO_4 のX線回折パターンを示す図。

【図5】本発明のリチウム二次電池の実施例1及び比較例1における電池の放電曲線を示す図。

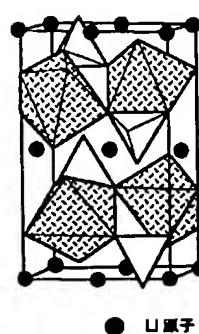
【符号の説明】

1	リン酸鉄リチウム系材料粉末
2	導電性微粒子
3	導電材
4	正極ペレット
5	金属リチウム負極
6	セパレータ
7	正極ケース
8	封口板
9	ガスケット

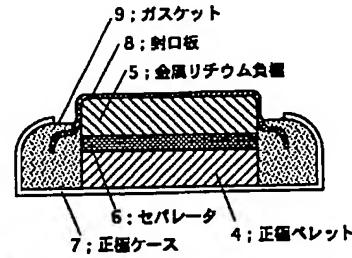
【図1】



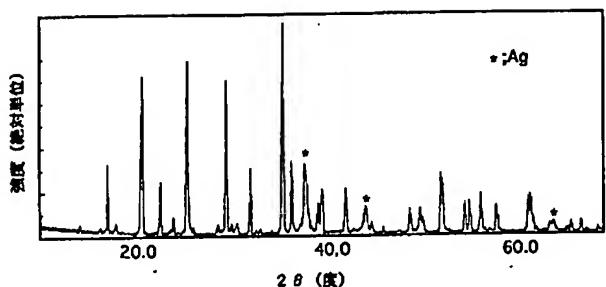
【図2】



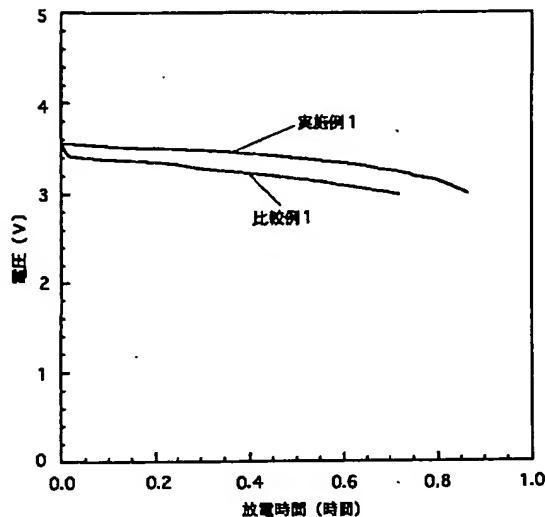
【図3】



【図4】



【図5】



フロントページの続き

(72)発明者 武井 弘次
東京都千代田区大手町二丁目3番1号 日
本電信電話株式会社内
(72)発明者 櫻井 庸司
東京都千代田区大手町二丁目3番1号 日
本電信電話株式会社内

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AM03 AM07 BJ02 BJ03 CJ22
DJ08 DJ16 EJ01 EJ04 HJ02
HJ18

TRANSLATION FROM JAPANESE

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(12) Unexamined Patent Gazette (A)
(11) Unexamined Patent Application (Kokai) No. 2001-110414 (P2001-110414A)
(43) Disclosure Date: April 20, 2001

(51)	Int. Cl. ⁷ :	Classification Symbols:	FI	Theme code (reference)
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(21) Application No.: 11-282445
(22) Filing Date: October 4, 1999
(71) Applicant: 000004226 (Nippon Telegraph and Telephone Corporation (NTT))
(72) Inventor: Masaya Takahashi
(72) Inventor: Shin'ichi Tobishima
(74) Agent: 100082717 (Masasue Amamiya, Patent Attorney)

(Continued on last page)

(54) [Title of the Invention] Lithium Secondary Cell Positive Electrode Active Material and Lithium Secondary Cell

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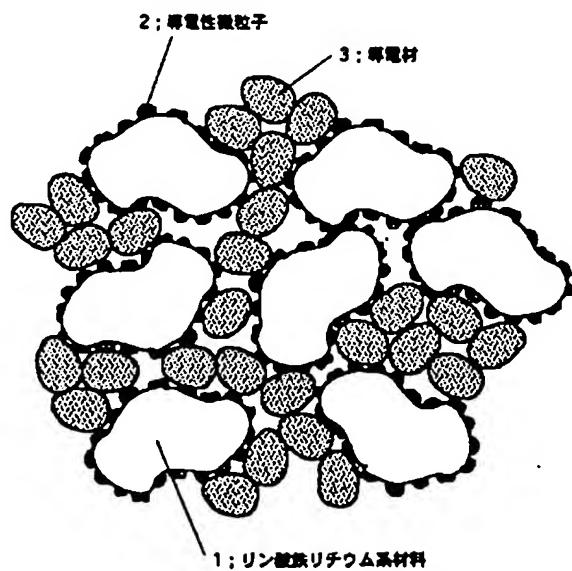
(54) [Title of the Invention] Lithium Secondary Cell Positive Electrode Active Material and Lithium Secondary Cell

(57) [Summary]

[Object] To increase charge-discharge capacity during high-current charging and discharging for a lithium secondary cell in which an inexpensive iron lithium phosphate material is used for the positive electrode.

[Means of Achievement] A pulverulent iron lithium phosphate material 1 whose olivine structure is expressed by the general formula $\text{Li}_2\text{Fe}_{1-y}\text{X}_y\text{PO}_4$ ($0 \leq y \leq 0.3$, $0 < z \leq 1$, X: at least one element selected from magnesium, cobalt, nickel, and zinc) is used as a carrier for an electroconductive pulverulent material 2 whose redox potential is higher than the redox potential of the iron lithium phosphate material as a lithium secondary cell positive electrode active material.

[Merits] Compared with constructing a cell by employing an unsupported iron lithium phosphate material, it is possible to obtain a cell whose charge-discharge capacity is considerable and decreases only slightly when the charge-discharge current is increased.



[Key to figure: 1: iron lithium phosphate material, 2: fine electroconductive particles, 3: conductive agent]

[Claims]

[Claim 1] A lithium secondary cell positive electrode active material, characterized in that a pulverulent iron lithium phosphate material whose olivine structure is expressed by the general formula $\text{Li}_z\text{Fe}_{1-y}\text{X}_y\text{PO}_4$ ($0 \leq y \leq 0.3$, $0 < z \leq 1$, X: at least one element selected from magnesium, cobalt, nickel, and zinc) is used as a carrier for fine electroconductive particles whose redox potential is higher than the redox potential of the iron lithium phosphate material as a lithium secondary cell positive electrode active material.

[Claim 2] A lithium secondary cell positive electrode active material as defined in Claim 1, characterized in that the fine electroconductive particles are composed of at least one element selected from silver, carbon, platinum, palladium, gold, iridium, aluminum, titanium, and tantalum.

[Claim 3] A lithium secondary cell, characterized in that the positive electrode active material is a lithium secondary cell positive electrode active material as defined in Claim 1 or 2, that the negative electrode active material is a material capable of storing and releasing lithium metal, lithium alloy, or lithium ions, and that the electrolyte is a material designed to allow the lithium ions to migrate and electrochemically react with the lithium secondary cell positive electrode active material or negative electrode active material.

[Detailed Description of the Invention]

[0001]

[Technological Field of the Invention] The present invention relates to a lithium secondary cell positive electrode active material and a lithium secondary cell, and more particularly to enhancing the electrical conductivity of a positive electrode active material in order to provide a cell with improved charge or discharge characteristics under high current conditions.

[0002]

[Prior Art] Lithium secondary cells whose negative electrode active material is capable of storing and releasing lithium metal, lithium alloy, or lithium ions are characterized by high voltage and excellent reversibility.

[0003] In particular, lithium ion secondary cells with lithium/transition metal complex oxides for the positive electrode active material, and carbonaceous materials for the negative electrode active material have higher discharge capacity at light loads than do conventional lead secondary cells, nickel-cadmium secondary cells, or the like, and are therefore widely used in portable phones, notebook computers, and other types of electronic equipment.

[0004] LiCoO₂ is primarily used as a positive electrode active material in current lithium ion secondary cells, but cobalt, which is a starting material for LiCoO₂, is scarce and can be produced in only a limited number of geographical regions, so using cobalt as a positive electrode active material for lithium ion secondary cells (the demand for which is projected to increase) is disadvantageous both in terms of price and in terms of stable supply of starting materials.

[0005] By contrast, it is clear from JP (Tokugan) 11-261394 and JP (Kokai) 9-134724 and 9-134725 that LiFePO₄ (obtained using abundant and inexpensive iron as a starting material) or a material in which the iron in the LiFePO₄ is partially substituted by other elements can also be used as a positive electrode active material for lithium secondary cells.

[0006]

[Problems Which the Invention Is Intended to Solve] These iron lithium phosphate materials are disadvantageous in the sense that lithium is introduced and desorbed at a low rate during the charging and discharging of cells and that these materials have higher electrical resistance than do conventional lithium metal oxides (LiCoO₂ and the like), causing resistance overvoltage or activation overvoltage to grow when the cells are charged or discharged under high current conditions, and preventing the cells from

maintaining adequate charge-discharge capacity levels because of the resulting reduction in cell voltage.

[0007] To address these problems, it has been proposed to increase the reaction-promoting surface area and to reduce the path of the electric current through particulate iron lithium phosphate materials by fashioning the iron lithium phosphate materials into smaller particles.

[0008] Secondary aggregation tends to occur, however, when a microparticulate iron lithium phosphate material is mixed with a conductive agent during electrode fabrication. Since the iron lithium phosphate material particles in the aggregated grains can come into contact with each other only along a limited number of points, the active material inside the aggregated grains fails to initiate reactions during cell charging and discharging, resulting in reduced charge-discharge capacity.

[0009] Consequently, an object of the present invention, which was perfected in order to address the problems of the prior art, is to achieve increased charge-discharge capacity during high-current charging and discharging in a lithium secondary cell in which an inexpensive iron lithium phosphate material is used for the positive electrode.

[0010]

[Means Used to Solve the Above-Mentioned Problems] Aimed at attaining the stated object, the lithium secondary cell positive electrode active material in accordance with the present invention is characterized in that a pulverulent iron lithium phosphate material whose olivine structure is expressed by the general formula $\text{Li}_z\text{Fe}_{1-y}\text{X}_y\text{PO}_4$ ($0 \leq y \leq 0.3$, $0 < z \leq 1$, X: at least one element selected from magnesium, cobalt, nickel, and zinc) is used as a carrier for an electroconductive pulverulent material whose redox potential is higher than the redox potential of the iron lithium phosphate material as a lithium secondary cell positive electrode active material.

[0011] The lithium secondary cell positive electrode active material in accordance with the present invention is also characterized in that the electroconductive pulverulent

material whose redox potential is higher than the redox potential of the iron lithium phosphate material as a lithium secondary cell positive electrode active material is composed of at least one element selected from silver, carbon, platinum, palladium, gold, iridium, aluminum, titanium, and tantalum.

[0012] In addition, the lithium secondary cell in accordance with the present invention is characterized in that the above-described lithium secondary cell positive electrode active material is used as a cell component, that the negative electrode active material is capable of storing and releasing lithium metal, lithium alloy, or lithium ions, and that the electrolyte is a material for allowing the lithium ions to migrate and electrochemically react with the positive electrode active material or negative electrode active material.

[0013] Fig. 1 is an enlarged, fragmentary, schematic cross-sectional view of a positive electrode obtained by mixing a conductive agent and the positive electrode active material used in a lithium secondary cell in accordance with the present invention. It can be seen in the drawing that when the iron lithium phosphate material 1 is reduced in diameter and mixed with the conductive agent 3 during electrode fabrication, aggregation is less likely to occur because supporting the fine electroconductive particles 2 on the surface of the pulverulent iron lithium phosphate material 1 substantially prevents the particles of the iron lithium phosphate material from coming into direct contact with each other.

[0014] Another feature is that because the fine electroconductive particles 2 in the aggregated grains form a path for the electric current even when aggregation occurs in the pulverulent iron lithium phosphate material 1, the electrical resistance inside the aggregated grains is markedly reduced and the active material inside the aggregated grains can be efficiently utilized during cell charging and discharging under high current conditions, making it possible to prevent the charge-discharge capacity from being reduced by the aggregation of the pulverulent iron lithium phosphate material 1.

[0015] The positive electrode of a conventional lithium secondary cell has considerable resistance in the small areas of direct contact between the active material particles and the conductive agent particles, or between the particles of the active material with high

electrical resistance. By contrast, the positive electrode active material of the present invention has low resistance at the surface of contact between the active material and the conductive agent 3 because this contact is formed between the fine electroconductive particles 2 and the conductive agent 3 or between the fine electroconductive particles 2, so smaller resistance variations are produced when the surface area of contact varies as a result of the active material expanding and contracting during repeated cell charging and discharging, less energy is lost during charging and discharging under high current conditions, and capacity is affected only slightly by such charging and discharging. These effects are believed to reinforce each other and to allow a lithium secondary cell in which an iron lithium phosphate material is used as the positive electrode active material to enhance its charge-discharge capacity during charging and discharging under high current conditions due to the use of the inventive positive electrode active material.

[0016] The iron lithium phosphate material used as a lithium secondary cell positive electrode active material in accordance with the present invention is a phosphate compound whose olivine structure is expressed by the general formula $\text{Li}_z\text{Fe}_{1-y}\text{X}_y\text{PO}_4$ ($0 < z \leq 1$, $0 < y \leq 0.3$). Element X is a material that remains electrochemically stable in a potential range between 3 V and 4 V in relation to the standard electrode potential of lithium metal when the element is a component of the phosphate compound. Specifically, X is at least one element selected from magnesium, cobalt, nickel, and zinc. Fig. 2 shows the olivine structure of LiFePO_4 . The solid circles show lithium atoms, the octahedrons represent irons surrounded by six oxygens, and the tetrahedrons indicate phosphors surrounded by four oxygens.

[0017] The material commonly referred to as iron lithium phosphate, expressed as LiFePO_4 ($z = 1$, $y = 0$), maintains its structure and does not allow any more lithium to be introduced. Using this iron lithium phosphate material for the positive electrode of a cell allows lithium to be removed from the positive electrode, causes the composition of the material to approach FePO_4 (the z-value to decrease) during charging, and allows the lithium in the electrolyte to be introduced into the positive electrode, and the composition to return to LiFePO_4 ($z = 1$), when the charged cell is discharged. A material with $z = 1$ is

preferred the most from the standpoint of cell discharge capacity and cell fabrication, but because the z-value continuously varies in the above-described manner, a material with a nonstoichiometric composition such as $z = 0.9$ can still yield a cell capable of operating by the same mechanism as iron lithium phosphate, which is a stoichiometric composition with $z = 1$. For this reason, the z in the above formula may vary within the range $0 < z \leq 1$.

[0018] In LiFePO₄, the lithium is desorbed and the iron ions alter their valence from two to three during charging. Such lithium desorption destabilizes the crystal structure (olivine structure) of the affected area, partially blocks the lithium migration routes, and makes it more difficult for the lithium inside the material to be desorbed. The iron is partially substituted by zinc and other elements electrochemically stable in a potential range between 3 V and 4 V in relation to the standard electrode potential of lithium metal when the element is a component of the phosphate compound, whereupon the elements substituted by zinc and other compounds remain unoxidized and retain their bivalent state during charging, and the lithium adjacent to the substituted elements also remains in the crystal without being desorbed. It is thus believed that the substituted areas are unlikely to alter their crystal structure during charging and that the lithium migration routes are preserved, resulting in enhanced capacity and improved cycle stability. It should be noted, however, that such undesorbed lithium does not contribute to charging or discharging, so cell capacity decreases when this type of substitution becomes excessively pronounced. For this reason, elemental iron should be substituted in an amount of 30% or less ($0 \leq y \leq 0.3$), preferably 10% to 30% ($0.1 \leq y \leq 0.3$), and ideally 10% to 20% ($0.1 \leq y \leq 0.2$) in order to achieve a capacity-enhancing effect when such substitutions are carried out.

[0019] According to the present invention, the surface of the iron lithium phosphate material is covered with the aforementioned fine electroconductive particles whose redox potential is higher than that of the iron lithium phosphate material used as the lithium secondary cell positive electrode active material. This is because the fine electroconductive particles prematurely initiate electrochemical reactions, electrical

conductivity is reduced by oxidation-induced dissolution, and the effect of depositing the fine electroconductive particles is lost when the electrochemical reactions of the fine electroconductive particles involving secondary lithium electrons are initiated at a lower potential than the redox potential (about 3.4 V) of the iron lithium phosphate material.

[0020] Such fine electroconductive particles may, for example, be composed of at least one element selected from silver, carbon, platinum, palladium, gold, iridium, aluminum, titanium, and tantalum. The working examples given below are described with reference to cases in which the aforementioned fine electroconductive particles are composed of metal materials such as silver, palladium, and platinum, or carbon materials such as acetylene black, although it is also possible to use metal materials such as gold, iridium, aluminum, titanium, and tantalum. Other examples of carbon materials include graphite and Ketjen black.

[0021] Adding a greater amount of fine electroconductive particles has no effect on allowing the material itself to contribute to the charge-discharge reactions, so the addition should be kept at 10% or less, and preferably 2% to 6%, because an excessively large addition will reduce the discharge capacity (per unit weight or volume) of a positive electrode active material as a whole when this material is a combination of an iron lithium phosphate material and fine electroconductive particles.

[0022] The diameter of the fine electroconductive particles should be no more than 1/10, and preferably 1/100 to 1/10, of the grain size of the iron lithium phosphate material. The fine electroconductive particles do not contribute to electrochemical reactions, and should therefore be deposited on the surface of the particulate iron lithium phosphate material uniformly and with minimal weight. This is because uniformly depositing coarse electroconductive particles on the surface of the particulate iron lithium phosphate material may produce an excessively large amount of such electroconductive particles and result in reduced energy density.

[0023] The working examples given below are described with reference to the use of positive electrodes in the form of molded pellets. It is also possible, however, to obtain a

positive electrode by a method in which a slurry is prepared by adding a positive electrode active material and a binder such as polyvinylidene fluoride to a solvent such as *N*-methyl-2-pyrrolidone, and a coated electrode is then fabricated by drying the resulting solution after applying it in the form of a thin coating to metal foil.

[0024] Although lithium metal is used below as the negative electrode active material, it is also possible to use lithium alloys; carbonaceous materials such as graphite and coke; metal oxides such as tungsten oxide, niobium oxide, vanadium oxide, and tin oxide; lithium/transition metal composite nitrides such as lithium manganese nitride, lithium cobalt nitride, and lithium iron nitride; metal chalcogenides such as iron sulfide and molybdenum sulfide; and the like.

[0025] Although the liquid electrolyte was obtained by dissolving LiPF₆ to a concentration of 1 mol/dm³ in an isovolumetric mixed solvent comprising ethylene carbonate and dimethyl carbonate, it is also possible to use electrolytes similar to those used in conventional nonaqueous lithium secondary cells.

[0026] Examples of suitable solvents include dimethoxyethane, 2-methyltetrahydrofuran, ethylene carbonate, methyl formate, dimethyl sulfoxide, propylene carbonate, acetonitrile, dimethyl carbonate, diethyl carbonate, and methyl ethyl carbonate, which can be used either alone or as mixtures of two or more components.

[0027] The following solutes can also be used in addition to the LiPF₆ employed in the working examples: LiClO₄, LiBP₄, LiAsF₆, LiCF₃SO₃, and the like. It is also possible to use polymer electrolytes, solid electrolytes, salts melting at normal temperature, and the like.

[0028] Various conventional materials can be used for the separators, cell cases, and other structural elements of cells. In addition, the working examples are described with reference to a coin shape as a possible cell configuration, but this shape is nonlimiting, and cylindrical, square, and other shapes may also be used.

[0029]

[Working Examples] Working examples of the present invention will now be described with reference to the accompanying drawings, but the present invention is not limited by these working examples.

[0030]

[Working Example 1] Fig. 3 is a cross-sectional view depicting the structure of a lithium secondary cell obtained in accordance with a working example of the present invention.

In Fig. 3, 4 is a positive electrode pellet, 5 a lithium metal negative electrode, 6 a separator, 7 a positive electrode housing, 8 a sealing plate, and 9 a gasket. The positive electrode active material contained in the positive electrode pellet 4 was prepared by the following method.

[0031] Lithium carbonate (Li_2CO_3), iron oxalate dihydrate ($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), and diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$) were first mixed as starting materials in a mortar in a molar ratio of 0.5:1:1 and baked for 24 hours in an argon atmosphere at 800°C to synthesize LiFePO_4 .

[0032] The synthesized LiFePO_4 powder was subsequently introduced and thoroughly stirred in a mixed solvent comprising water and ethanol in a volume ratio of 1:1, and silver nitrate (AgNO_3) was added under stirring such that the weight of contained silver ions was 5% of the weight of LiFePO_4 .

[0033] Acetaldehyde was then added under continued stirring in an amount of 20 mL per gram of AgNO_3 , and silver was allowed to precipitate on the LiFePO_4 powder. The product was filtered and dried, yielding a positive electrode active material.

[0034] Fig. 4 is an X-ray diffraction chart of the resulting positive electrode active material. Metallic silver peaks, marked by asterisks in Fig. 4, were observed in addition to the LiFePO_4 peaks. In addition, electron microscope observations and EPMA measurements confirmed that fine silver particles whose grain size was about 1/20 that of the LiFePO_4 powder were supported in dispersed form on the LiFePO_4 powder.

[0035] The positive electrode active material (70 wt%), acetylene black as a conductive agent (25 wt%), and polytetrafluoroethylene as a binder (5 wt%) were blended together into a clayey mass, calendered with biaxial rolls to a thickness of about 0.6 mm, and stamped with a punch into a disk with a diameter of 15 mm, yielding a positive electrode pellet 4.

[0036] An assembly obtained by forcing a lithium metal negative electrode 5 into a stainless steel sealing plate 8 was subsequently introduced into the concavity of a polypropylene gasket 9, a microporous polypropylene separator 6 and a positive electrode pellet 4 were placed on the negative electrode in the order indicated, the assembly was impregnated with a liquid electrolyte obtained by dissolving LiPF₆ in an isovolumetric mixed solvent (ethylene carbonate and dimethyl carbonate) in a concentration of 1 mol/dm³, and the impregnated assembly was covered with a stainless steel positive electrode housing 7 and crimped, yielding a coin-shaped lithium secondary cell with a thickness of 2 mm and a diameter of 23 mm.

[0037] The charge-discharge characteristics of the resulting cell were evaluated by charging and discharging the cell at an end-of-charge voltage of 4.0 V, an end-of-discharge voltage of 3.0 V, and a high current (5 mA).

[0038] Fig. 5 shows a voltage curve obtained when the cell was discharged at the 5-mA current. The voltage curve was substantially the same as that obtained by the low-current charging and discharging of a conventional cell whose positive electrode is composed of an iron lithium phosphate material not coated with fine electroconductive particles and whose negative electrode is composed of lithium metal, and it was confirmed that the cell was charged and discharged by the oxidation and reduction of iron ions and that the supported electroconductive material did not undergo any oxidation or reduction.

[0039] The charge-discharge capacity was 5.6 mAh at a current of 1 mA, and 4.3 mAh at a current of 5 mA. Table 1 shows the discharge capacities obtained when the cell was tested by being charged and discharged at various currents.

[0040]

[Table 1]

Discharge voltage and discharge capacity of cells in working and comparative examples

Working and comparative examples	Discharge capacity during 1-mA discharge (mAh)	Discharge capacity during 5-mA discharge (mAh)
Working Example 1	5.6	4.3
Comparative Example 1	5.2	3.6
Working Example 2	5.7	4.4
Working Example 3	5.4	4.0
Working Example 4	5.5	4.1

[0041]

[Comparative Example 1] The following method was used to prepare LiFePO₄ as a positive electrode active material on which no electroconductive material was supported.

[0042] Lithium carbonate (Li₂CO₃), iron oxalate dihydrate (FeC₂O₄ · 2H₂O), and diammonium hydrogen phosphate ((NH₄)₂HPO₄) were first mixed as starting materials in a mortar in a molar ratio of 0.5:1:1 and baked for 24 hours in an argon atmosphere at 800°C.

[0043] A positive electrode pellet and a coin-shaped cell were then fabricated using the resulting positive electrode active material in accordance with the same method as in Working Example 1.

[0044] Charge-discharge characteristics were evaluated under the same conditions as in Working Example 1 and it was found that the discharge capacity was 5.2 mAh at a current of 1 mA, and 3.6 mAh at a current of 5 mA, and that in both cases the discharge capacity was lower than in Working Example 1 and that the reduction in capacity was particularly pronounced when the test was conducted at a constant current of 5 mA.

[0045] A voltage curve obtained when the cell was discharged at a current of 5 mA is shown in Fig. 4 together with the curve of Working Example 1. In addition, discharge

capacities achieved in the charge-discharge tests at various currents are shown in Table 1 together with the values for Working Example 1.

[0046]

[Working Example 2] The positive electrode active material contained in the positive electrode pellet was prepared by the following method.

[0047] Lithium carbonate (Li_2CO_3), iron oxalate dihydrate ($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), and diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$) were first mixed as starting materials in a mortar in a molar ratio of 0.5:1:1 and baked for 5 hours in an argon atmosphere at 350°C.

[0048] Acetylene black (from Denki Kagaku Kogyo) was then added in an amount of 10 g per gram of starting material, the ingredients were thoroughly mixed, and the mixture was baked for 24 hours in an argon atmosphere at 800°C.

[0049] A positive electrode pellet and a coin-shaped cell were then fabricated using the resulting positive electrode active material in accordance with the same method as in Working Example 1.

[0050] Charge-discharge characteristics were evaluated under the same conditions as in Working Example 1 and it was found that the discharge capacity was 5.7 mAh at a current of 1 mA, and 4.4 mAh at a current of 5 mA, and that in both cases the discharge capacity was higher than in Comparative Example 1.

[0051] Discharge capacities achieved in the charge-discharge tests at various currents are shown in Table 1 together with the values for Working Example 1 and Comparative Example 1.

[0052]

[Working Example 3] The positive electrode active material contained in the positive electrode pellet was prepared by the following method.

[0053] Lithium carbonate (Li_2CO_3), iron oxalate dihydrate ($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), and diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$) were first mixed as starting materials in a mortar in a molar ratio of 0.5:1:1 and baked for 24 hours in an argon atmosphere at 800°C to synthesize LiFePO_4 .

[0054] The synthesized LiFePO_4 powder was subsequently pulverized and introduced into an acetonitrile solution of palladium acetate ($\text{Pd}(\text{OCOCH}_3)_2$), and the product was thoroughly stirred, filtered, and dried, causing the $\text{Pd}(\text{OCOCH}_3)_2$ to deposit on the LiFePO_4 powder.

[0055] The product was baked for 5 hours at 250°C in an argon atmosphere to pyrolyze the $\text{Pd}(\text{OCOCH}_3)_2$ and to fabricate a positive electrode active material by supporting palladium on the LiFePO_4 powder.

[0056] A coin-shaped cell was then fabricated using the resulting positive electrode active material in accordance with the same method as in Working Example 1.

[0057] Charge-discharge characteristics were evaluated under the same conditions as in Working Example 1, and it was found that the discharge capacity was 5.4 mAh at a current of 1 mA, and 4.0 mAh at a current of 5 mA, and that in both cases the discharge capacity was higher than in Comparative Example 1.

[0058] Discharge capacities achieved in the charge-discharge tests at various currents are shown in Table 1 together with the values for Comparative Example 1 and Working Examples 1 and 2.

[0059]

[Working Example 4] The positive electrode active material contained in the positive electrode pellet was prepared by the following method.

[0060] Lithium hydroxide monohydrate ($\text{LiOH} \cdot \text{H}_2\text{O}$), iron oxalate dihydrate ($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), and diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$) were first mixed as starting

materials in a mortar in a molar ratio of 1:1:1 and baked for 24 hours in an argon atmosphere at 800°C to synthesize LiFePO₄.

[0061] Pulverulent titanium (300 mesh) was subsequently added to the resulting LiFePO₄ powder in an amount of 6 g per 100 g of LiFePO₄, and the ingredients were mixed in a mortar, introduced into a planetary ball mill made of agate, and pulverized and mixed for 20 minutes, causing the microparticulate platinum to disperse and deposit on the LiFePO₄ powder.

[0062] A coin-shaped cell were then fabricated using the resulting positive electrode active material in accordance with the same method as in Working Example 1.

[0063] Charge-discharge characteristics were evaluated under the same conditions as in Working Example 1 and it was found that the discharge capacity was 5.5 mAh at a current of 1 mA, and 4.1 mAh at a current of 5 mA. Discharge capacities achieved in the charge-discharge tests at various currents are shown in Table 1 together with the values for Working Examples 1–3 and Comparative Example 1.

[0064]

[Merits of the Invention] It follows from the above description that by using a material obtained by supporting fine electroconductive particles on a pulverulent iron lithium phosphate material as a positive electrode active material for the lithium secondary cell according to the present invention, it is possible to achieve a higher charge-discharge capacity than the one provided by a cell with an unsupported iron lithium phosphate material, and that the resulting cell decreases its charge-discharge capacity to a lesser degree when the charge-discharge current is increased.

[0065] It is thus possible to obtain a more economical lithium secondary cell with better cell characteristics.

[Brief Description of the Figures]

[Figure 1] An enlarged, fragmentary, schematic cross-sectional view of a positive electrode obtained by mixing a conductive agent and a lithium secondary cell positive electrode active material according to the present invention.

[Figure 2] A schematic depicting the olivine structure.

[Figure 3] A cross-sectional view depicting the structure provided by a working example of a lithium secondary cell in accordance with the present invention.

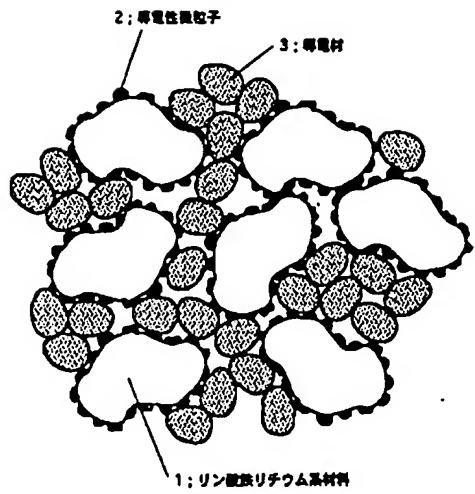
[Figure 4] A diagram depicting an X-ray diffraction pattern of an LiFePO₄ product coated on the surface with fine silver particles and used as a positive electrode active material in accordance with Working Example 1 of the inventive lithium secondary cell.

[Figure 5] A diagram depicting the discharge curves of cells belonging to Working Example 1 and Comparative Example 1 and representing the lithium secondary cells of the present invention.

[Key]

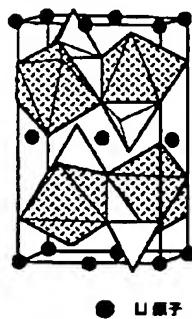
1: pulverulent iron lithium phosphate material, 2: electroconductive microparticulate material, 3: conductive agent, 4: positive electrode pellet, 5: lithium metal negative electrode, 6: separator, 7: positive electrode housing, 8: sealing plate, 9: gasket

[Figure 1]



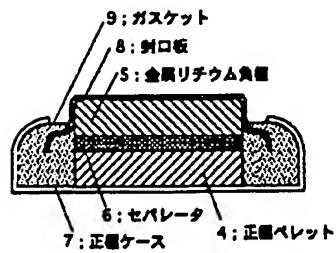
[Key to figure: 1: iron lithium phosphate material, 2: fine electroconductive particles,
3: conductive agent]

[Figure 2]



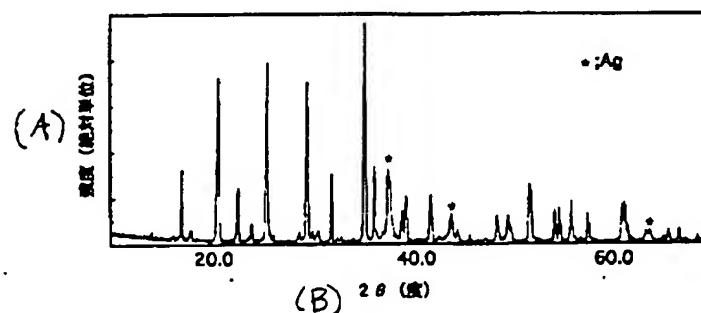
[Key to figure: Li atom]

[Figure 3]



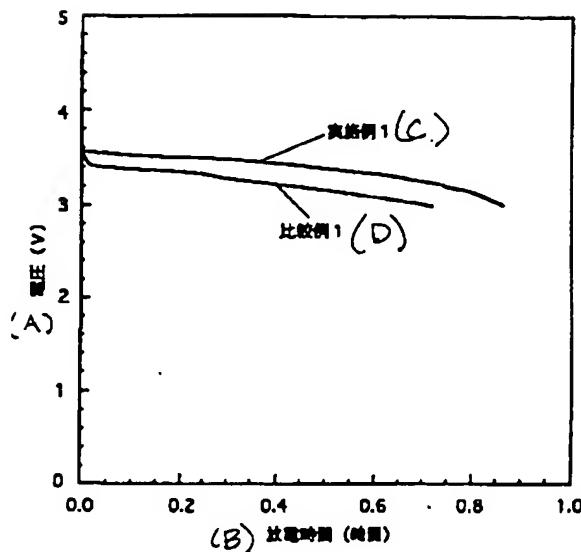
[Key to figure: 4: positive electrode pellet, 5: lithium metal negative electrode, 6: separator, 7: positive electrode housing, 8: sealing plate, 9: gasket]

[Figure 4]



[Key to figure: (A) Intensity (relative units), (B) 2θ (degrees)]

[Figure 5]



[Key to figure: (A) Voltage (V), (B) Discharge time (hours), (C) Working Example 1,
(D) Comparative Example 1]

(Continued from front page)

(72) Inventor: Koji Takei

(72) Inventor: Yoji Sakurai

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